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The impedance of anodic processes on passive NiSi-electrode in sulfuric fluoride containing electrolyte*

The mechanism and kinetics of anodic oxidation of the Ni-Si electrode in solutions of 0.5 M H_2SO_4 + (0,005 – 0,05)M NaF in the passive state were investigated by methods of polarization and impedance measurements. The impedance spectra are interpreted on the assumption about the formation of the bilayer oxide film on the surface of the silicide nickel, the outer layer which has a porous structure. The growth of the porous layer with the increase of the electrode potential in the investigated solutions is linearly (constant anodizing is 2.2 nm/V). The increase in NaF concentration leads to a decrease in the thickness of the porous layer. The growth of the barrier layer of the oxide film was described in the framework of the model of point defects. The diffusion coefficient of oxygen vacancies inside the barrier layer of the film is $8.5 \cdot 10^{-16} \text{ cm}^2/\text{s}$ and varies weakly with the potential and the content of sodium fluoride in solution. Microscopic and profilometric studies show the development of the surface of the NiSi electrode during anodic etching.

Keywords: the method of impedance measurements; two layer oxid; metal monosilicic.

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Introduction

In the study of anodic processes on the mono-silicides of metals of the iron triads in solution of 0.5 M H_2SO_4 was found that a factor contributing to the high chemical resistance of the passive FeSi, CoSi, and NiSi in sulfuric electrolyte is the surface chemically stable in acidic media film, similar in composition to SiO_2 , for which characteristics such as impedance, electrical resistance, resistivity and uniformity have a maximum

value approximately in the middle of the passivation field [1–4].

However, when the content in the solution of hydrofluoric acid or its salts passivation influence of silicon dioxide is weakened: fluosilicic acid or a soluble ferrosilicates [4–7] are formed in the interaction of SiO_2 with HF or F-ions. The aim of the present study is to examine the concentration effect of sodium fluoride on the kinetics and mechanism of anodic

oxidation of the NiSi electrode in sulfuric acid solution in the passive state.

Experimental technique

The material for investigation was monosilicic nickel, which was obtained by the Czochralski method from a silicon KPZ-1 (99.99 wt. % Si) and electrolytic nickel N-0 (99.99 wt. % Ni). The electrochemical measurements were performed in solutions of 0.5 M H_2SO_4 + (0,005 – 0,05)M NaF at room temperature (~20 – 22 °C) in conditions of natural aeration in the fluoroplastic cell using a potentiostat-galvanostat with built-in frequency analyzer Solartron 1280C (Solartron Analytical).

For the preparation of solutions the deionised water was used (resistivity 18.2 MOhm·cm) and reagents H_2SO_4 of brand “c.p.” and NaF of brand “c.f.a.”. All potentials in this work are presented in comparison to the normal hydrogen electrode. Before measurement the working electrode surface was polished with abrasive papers with consequent reduction of grain size, degreased with etha-

nol, rinsed with working solution. After immersion in the solution the electrode was held at open-circuit potential before the establishment of the stationary value of the potential, then the current-voltage curves and impedance spectra were took. The range of frequency f ($\omega/2\pi$) used in the impedance measurement was from 20 kHz to (0,005 – 0,002) Hz, the amplitude of the AC signal was (10 to 20) mV.

The morphology of the sample surface before and after electrochemical testing was examined using a scanning electron microscope S-3400N (Hitachi). The images were obtained in a high vacuum at an accelerating voltage of 10 kV in the mode scattering of secondary electrons.

The study of micro-roughness of the electrode surface was carried out at the interference microscope - non-contact profilometer “New View 5000” (Zygo).

Results and discussion

The anodic potentiostatic curves of NiSi electrode in solutions of 0.5 M H_2SO_4 + (0 – 0,05)M NaF are shown in Fig.1. In the potential range from 0.40 to 1.70 V, corresponding to the passive state, the polarization curves of NiSi there is a noticeable growth of i with increasing electrode polarization and with increasing the content of sodium fluoride in solution.

In the passive potential state, the impedance hodographs NiSi electrode in the investigated solutions consist of the capacitive semicircle at high frequencies and of the inclined line at low frequencies (Fig. 2).

The equivalent electric circuit describing the presence on the surface of the electrode the double-layer passivating film, consisting of an inner barrier and outer porous layers (Fig. 3) was used for the simulation of impedance spectra of NiSi (Fig. 2). The film growth is associated with the transfer of the defects inside the barrier layer, which through the pores of the outer layer the electrolyte is accessed. At the interface of the barrier layer/electrolyte interface as a result of interaction of the substance of the oxide film with hydrofluoric acid is place of its partial transition to the solution and the

formation of pores. In the circuit in Fig. 3: R_s is resistance of the electrolyte between the spout of the capillary Loggia and the working electrode surface, R_1 is the resistance of the electrolyte in the pores of the outer layer, R_2 is the resistance of charge transfer, Z_d is the Warburg impedance describing the migration of defects within the barrier layer, the elements of constant phase CPE_1 and CPE_2 are modeling the heterogeneous capacity of the outer layer of an oxide film and boundary barrier layer/electrolyte interface, respectively.

The parameter χ^2 for the equivalent circuit in Fig. 3 takes values $(8-20) \cdot 10^{-5}$, which show a good correlation between the model and experimental data.

It follows from calculated by the equivalent circuit data in Fig. 3, while developing the capacity NiSi electrode in all solutions investigated, the thickness of the outer porous layer increases with E , approximately linearly, with the increase of porosity outstripping the growth of the

layer thickness. Under the assumption that the basis of oxide film on the surface of the silicide of nickel in fluoride containing electrolyte is NiO (or hydrated oxide of $Ni(OH)_2$), estimated the thickness d of the porous layer of the oxide film: constant growth ($K = dd/dE$) of the porous layer of the oxide film in the potential range from 0.8 to 1.6V equal to 2.2 nm (the thickness of the porous layer varies from 3.2 to 5.0 nm for solutions with different concentrations of NaF). If we assume that the passive film is a mixed oxide and along with the nickel oxide also contains a certain amount of silicon dioxide, the constant anodizing will be somewhat less. The increasing of the concentration of sodium fluoride leads to a slight reduction in the thickness of the porous layer of the oxide film that, apparently, is connected with the dissolution of the substance of the film in the presence of HF. The thickness of the barrier layer also increases with increasing E . The coefficient of the diffusion of oxygen vacancies D inside barrier layer of the passivating film on

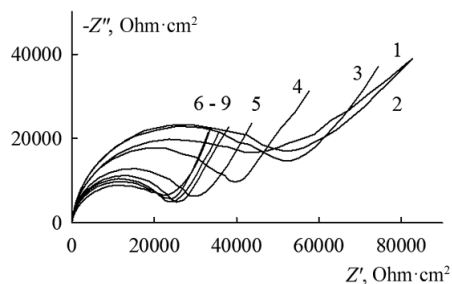


Fig. 1. Anodic potentiostatic curves of NiSi in 0.5 M H_2SO_4 + NaF, M: 1 – 0; 2 – 0,005; 3 – 0,01; 4 – 0,02; 5 – 0,05

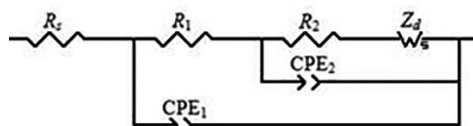


Fig. 3. An equivalent electric circuit for NiSi in 0.5 M H_2SO_4 + (0,005 – 0,05) M NaF in the passive state

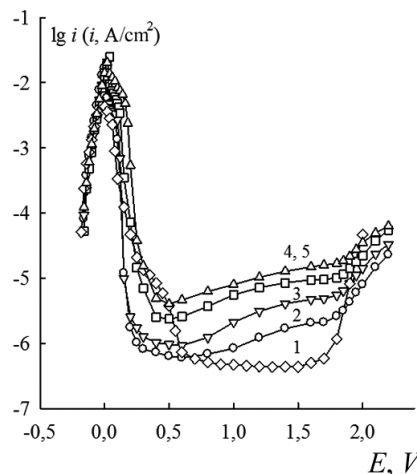


Fig. 2. Impedance spectra NiSi in 0.5 M H_2SO_4 + 0.02 M NaF at E , In: 1 – 0,40; 2 – 0,50; 3 – 0,60; 4 – 0,80; 5 – 1,00; 6 – 1,20; 7 – 1,40; 8 – 1,60; 9 – 1,70

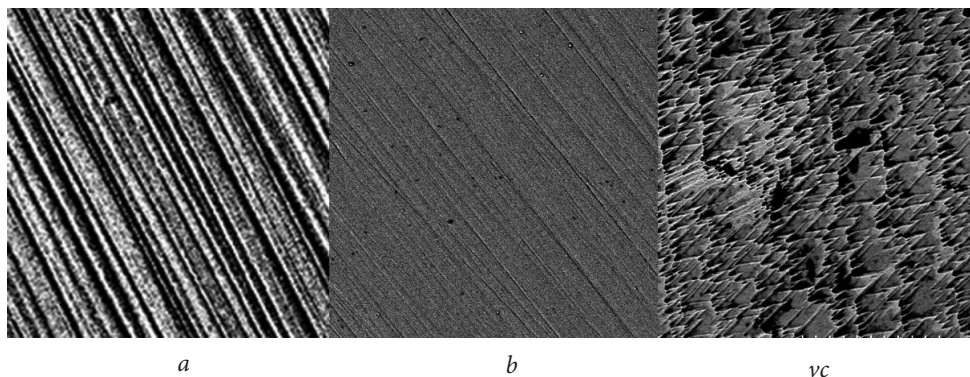


Fig. 4. Photomicrographs of the surface of the NiSi ($\times 700$) before (a) and after anodic etching in $0.5 \text{ M H}_2\text{SO}_4$ (b) and $0.5 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M NaF}$ (b) at $E = 1.2 \text{ V}$

the NiSi in the solution of $0.5 \text{ M H}_2\text{SO}_4 + 0.02 \text{ M NaF}$ at $E = 1.2 \text{ V}$ is $8.5 \cdot 10^{-16} \text{ cm}^2/\text{s}$ and varies weakly with increasing electrode polarization and the content of sodium fluoride in solution. A slight increase of the diffusion coefficient (but very weak) when the concentration of sodium fluoride in solution, probably due to the increase of defects in the structure of the barrier layer film formed in the presence of fluoride.

The microscopic examination NiSi before and after electrochemical testing shows that the anodic etching of silicide at E the passive condition in $0.5 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M NaF}$ leads to a significant development of the electrode surface (Fig. 4 presents the comparison of photographs of the electrode surface before and after anodic etching in bestrides and fluoride containing solutions).

Conclusion

The investigation of the anodic behavior of NiSi electrode in sulfuric electrolyte containing a variable amount of hydrofluoric acid shows that the presence of HF in solution exerts a strong influence on current-voltage and impedance cha-

The development of the surface of the electrode in sulfuric non-fluoride electrolyte may be due to restroom in the potential region of active dissolution and of active-passive transition. The introduction to the solution of sodium fluoride leads to an even more substantial irritation of the electrode surface due to dissolution of the oxides NiO and SiO_2 in the presence of fluoride formed during anodic oxidation of NiSi in the passive state.

The results of measurement of micro-roughness of the surface of the NiSi electrode fully correlate with the microscopic studies.

The values of R_a and rms change as follows: $R_a \text{ (nm)}/\text{rms (nm)} = 25,5/34,3$ (initial sample) : $79,8/119,4$ p (anodic etching in $0.5 \text{ M H}_2\text{SO}_4$ at $E = 1.2 \text{ V}$) : $957,5/1240,8$ (anodic etching in $0.5 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M NaF}$ at $E = 1.2 \text{ V}$).

acteristics of the silicide. The latter is evident in the substantial weakening of the passivating action of oxygen-containing compounds of the alloy components and activation NiSi of dissolution.

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